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DETERMINATION OF WATER IN PYROTECHNIC MIXTURES BY GAS CHROMATOGRAPHY

by

John M. Bane

Directorate of Development and Engineering

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DEPARTMENT OF THE ARMY
Headquarters, Edgewood Arsenal
Aberdeen Proving Ground, Maryland 21010

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A procedure, using gas chromatography, has been developed for the analysis of water in pyrotechnic mixtures. Regression analysis of data indicated that with benzene as internal standard, weight of water could be determined to within ±0.001 gram in the examined range of 0.001 to 0.022 grams of water. Water was extracted from the pyrotechnic mix with absolute methanol. An internal standard (benzene or n-pentane) was added to the resultant slurry. After solids had settled, a sample of the clear liquid for resolution and analysis was injected into a gas chromatograph fitted with a Porapak Q filled column. Standard solutions, prepared with the same ratio of internal standard to methanol as the methanol extract of pyrotechnic mix and various amounts of water, were

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) resolved under similar conditions on the chromatograph. A calibration curve was prepared by plotting weight of water added to each standard versus the respective ratio, R (area water peak/area internal standard peak – corrected to a common weight of internal standard). Weight of water in the pyrotechnic material was found by comparing its R value to the curve. Several facts indicate that accurate and reproducible results may be obtained by this procedure. When data from similar tests were plotted, the curves were very nearly parallel. Individual data points showed good fit to respective regression curves. The 99% confidence bands for the combined data from two tests were calculated with maximum variation from the regression curve being less than 3%. The internal standard technique appears to be a good general procedure for handling pyrotechnic mixtures, especially starter mixes that contain relatively little material, other than water, that is soluble in methanol. Mixes that contain methanol solubles in addition to water may be analyzed by this method provided their chromatographic peaks do not overlap the water and internal standard peaks.

SUMMARY

A procedure, using gas chromatography, has been developed for the analysis of water in pyrotechnic mixtures. Regression analysis of data indicated that with benzene as internal standard, weight of water could be determined to within ±0.001 gram in the examined range of 0.001 to 0.022 grams of water.

Water was extracted from the pyrotechnic mix with absolute methanol. An internal standard (benzene or n-pentane) was added to the resultant slurry. After solids had settled, a sample of the clear liquid for resolution and analysis was injected into a gas chromatograph fitted with a Porapak Q filled column.

Standard solutions, prepared with the same ratio of internal standard to methanol as the methanol extract of pyrotechnic mix and various amounts of water, were resolved under similar conditions on the chromatograph. A calibration curve was prepared by plotting weight of water added to each standard versus the respective ratio, R (area water peak/area internal standard peak – corrected to a common weight of internal standard). Weight of water in the pyrotechnic material was found by comparing its R value to the curve.

Several facts indicate that accurate and reproducible results may be obtained by this procedure. When data from similar tests were plotted, the curves were very nearly parallel. Individual data points showed good fit to respective regression curves. The 99% confidence bands for the combined data from two tests were calculated with maximum variation from the regression curve being less than 3%.

The internal standard technique appears to be a good general procedure for handling pyrotechnic mixtures, especially starter mixes that contain relatively little material, other than water, that is soluble in methanol. Mixes that contain methanol solubles in addition to water may be analyzed by this method provided their chromatographic peaks do not overlap the water and internal standard peaks.

PREFACE

The work described in this report was conducted under Task 1W162116A08104, Thermal Dissemination of Chemical Agents. This work was started in April 1971 and completed in July 1971. The experimental data are contained in notebook 8263.

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Acknowledgment

The author wishes to acknowledge the technical assistance of Messrs. Stanley Kramer, Robert Valis, and Merrill Milham.

CONTENTS

DETERMINATION OF WATER IN PYROTECHNIC MIXTURES BY GAS CHROMATOGRAPHY

I. INTRODUCTION.

The presence of excess water in a pyrotechnic mixture may cause the mixture to malfunction or misfire when used in munitions. Previous work by the Ground Munitions Branch has shown that as little as 0.5% of water in a CS pyrotechnic material caused burning time to exceed the specification limit. Water may change the composition of a mix through corrosion of metal containers and hydrolysis of mix components and thereby alter both its ignition temperature and burning characteristics.

At present, the water content of a pyrotechnic mixture is found either by drying a sample and equating weight loss with water content or by titrating it with the Karl Fischer reagent. Objections to the determination of water by drying are: (1) the procedure is nonspecific for water, (2) it measures total volatiles including sublimates such as CS, and (3) it takes a matter of days to complete an analysis. The Karl Fischer reagent is also nonspecific for water. It reacts with some materials commonly found in pyrotechnics (e.g., zinc oxide and potassium chlorate); therefore, these mixtures cannot be titrated directly with the reagent. Water must be extracted with a suitable solvent before the amount can be determined. The Karl Fischer reagent is obnoxious to handlers as it contains pyridine, sulfur dioxide, and iodine. Also, extra skill is required to obtain reproducible results with the reagent because of its extreme sensitivity to water.

A procedure, using gas chromatography, has been developed for the determination of water in pyrotechnics. This procedure was patterned, in general, after the internal standard technique of Hogan *et al.*[1] in which water was determined in a liquid containing methanol as internal standard after its resolution on a Porapak Q column.

In this procedure, methanol was used to extract water from a pyrotechnic mix, and a known quantity of benzene or n-pentane was added to the extract as internal standard. After resolution of the extract by gas chromatography, water was found by comparison of the rates, R (area water peak/area internal standard peak – corrected to a common weight of internal standard) to that of standard solutions. Standard solutions were prepared to contain the same ratio of internal standard to methanol as the mix extract and various amounts of water. Weight of water added (X) to each standard was plotted versus the respective ratio, R, to obtain a reference curve.

Potential areas of use for this procedure are: in quality control tests in the manufacture of pyrotechnic mixes, in surveillance analysis of munitions, and in the determination of change in the composition of a mix as a function of time or storage conditions.

II. EXPERIMENTATION

A. Equipment.

A Hewlett Packard 720 dual column chromatograph equipped with a thermal conductivity detector was used throughout the work. An Infotronics Digital Readout System, Model CRS-108, connected to the output of the thermal conductivity detector, integrated peak areas and printed out results in digital form.

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[1] Hogan, J. M., Engle, R. A., and Stevenson, H.F. Anal. Chem. *42*,249 (1970).

Sample injections were made with a 100-μl, gas-tight Hamilton syringe.

Volumetric flasks, previously dried in an oven and cooled in a desiccator, were used for the preparation of solutions. These flasks were stoppered with dry, sleeve-type serum stoppers.

B. Column Preparation.

The column, a 6-foot length of 0.25-inch-diameter stainless steel tubing packed with 80 to 100 mesh Porapak Q polymer beads, was purchased from Waters Associates, Inc. The Porapak Q, washed successively with 75-ml aliquots of methanol, water, 1:4 hydrochloric acid, water, methanol and acetone, was then air dried before it was packed in the column. Prior to use, the column was conditioned for 4 hours at 230°C with a helium flow of 60 ml/min.

C. Materials.

Distilled water and reagent grades of absolute methanol, benzene, and n-pentane were used to prepare the solutions.

D. Procedure.

1. Calibration Curves.

Standard solutions that served as simulated extracts of pyrotechnic mixes were prepared in 50-ml volumetric flasks. Flasks were filled to the mark with absolute methanol and were immediately capped with serum stoppers to prevent methanol from absorbing atmospheric moisture. An internal standard, either 50 μl of benzene or 100 μl of n-pentane, was added to each flask. The hydrocarbon was drawn into the syringe so that a few microliters of air was at the bottom; the excess liquid was wiped from the outside with a tissue. (The air pocket served as a cushion in preventing loss of hydrocarbon by evaporation or from bumping the syringe plunger.) After the syringe and contents had been weighed to 5 decimal places on a semimicro analytical balance, internal standard was injected into the methanol through the serum cap. To avoid loss of contents, a few microliters of air was pulled into the syringe before the needle was withdrawn from the cap. The syringe was reweighed and difference between the first and the second weighings was used as weight of internal standard added. Weight of water added to each flask was determined by the procedure used for the internal standard. Change in volume of the 50 ml of methanol by the additions of water and internal standard was considered negligible, and was thus ignored. After the additions of water and internal standard, the methanolic solutions were shaken vigorously several minutes to dissolve the water.

2. Procedure for Pyrotechnic Mixes.

A 5- to 10-gram sample of pyrotechnic mixture was weighed to the nearest 0.1 mg into a dried Erlenmeyer flask. A 50-ml sample of methanol (from the same bottle used to prepare standards) and a dried magnetic stirring bar were added to the mix. The flask was tightly stoppered and the contents were stirred magnetically for about 1 hour to attain equilibrium. (Extraction time depended on the physical condition of the mix and had to be determined empirically.) A predetermined amount of internal standard was added to the mix. The flask was restoppered and the mixture was stirred for several more minutes. After the reaction mixture had stood for 0.5 hour in the immediate area of the chromatograph to permit solids to settle, the clear supernatant liquid was used for analysis.

The chromatograph and integrator were allowed to stabilize at operating conditions for at least 0.5 hour prior to injection of the first sample. Before entering the chromatograph, helium carrier gas was dried by traveling through a tube filled with molecular sieves.

The syringe used to inject samples into the chromatograph was washed six or eight times with absolute methanol from the bottle of alcohol used to prepare standards before being put into a sample. It was flushed three times with the sample to be injected. A sample of the desired volume was drawn into the syringe, and approximately 1μ of air was drawn in behind it. Each sample was injected into the chromatograph smoothly and as one slug so that only one peak would appear for each constituent present.

During the first part of the run, the chromatograph was operated in the isothermal mode to maintain initial column temperature for the separation of water from methanol. Immediately after the front edge of the methanol peak appeared, the chromatograph was reset to the programmed temperature mode. The column was heated at a rate of 30°C per minute to an upper temperature of 230°C and held there to decrease retention time of the internal standard.

III. RESULTS.

A. Experimental Data.

Table I lists weights of reagents, chromatographic conditions, and experimental results for solutions which contained n-pentane as internal standard. Figure 1 is a graphic presentation of the weight of water added (X) to each standard compared to the ratio, R. Most of the data points fell on or near a straight line when plotted, and the curves from different runs were very nearly parallel.

Two parallel lines were obtained when data from test 109 was plotted. Slopes of 16.95 and 16.91, respectively, were obtained for top and bottom curves. The break in the curve was attributed to response to a broken wire in the coarse adjustment circuit.

In subsequent work (tests 118 and 120), benzene (50 μl) was substituted for n-pentane as internal standard because of its higher boiling point, 80.1°C (n-pentane bp, 36.1°C). Experimental results from tests 118 and 120 are given in table II.

B. Replicate Analyses.

In test 119, four replicate water analyses were run on the standard solutions prepared for test 118 so that reproducibility of results obtainable with a single set of standards could be observed. Chromatographic conditions were similar for both tests. Results from test 119 and the averaged results from tests 118 and 119 are shown in table III for comparison. The averaged results from tests 118 and 119 showed a general increase in the value of R over that of test 118; therefore, it was concluded that the water content of the standards increased with use.

A new bottle of methanol that contained less water than that used for test 118 was used to prepare test 120 standards. Otherwise (with the exception of sample size), all other chromatographic conditions were similar to those in tests 118 and 119. When test results were plotted for test 120 (see figure 2), a very good line was obtained that was very nearly parallel to the curve for averaged results of tests 118 and 119. Curve 120 was also closer to the origin as

Table I. Water in Methanol/n-Pentane Internal Standard

Test	Sample No.	n-Pentane	Water (X)	R′[a]	R[b]	Area water peak[a] / Area n-pentane peak
		gm	gm			
108[c]	2	0.06247	0.02612	1.1717	1.1602	7856/6705
	3	0.06299	0.05910	1.3285	1.3264	12728/9581
	4	0.06235	0.07731	1.7585	1.7379	17010/9673
	5	0.06262	0.10234	2.1740	2.1578	20703/9523
109[d]	2	0.06311	0.02657	0.8743	0.8746	6113/6992
	3	0.06341	0.05169	1.2929	1.2995	9337/7222
	4	0.06315	0.07659	1.8377	1.8394	12893/7016
	5	0.06324	0.10296	2.2811	2.2865	16182/7094
110[c]	1	0.06377	0.01274	0.7268	0.7346	6386/8786
	2	0.06319	0.00718	0.6877	0.6888	5235/7612
	3	0.06340	0.00364	0.5650	0.5678	5206/9215
111[c]	1	0.06269	0.00092	0.5845	0.5808	5451/9325
	2	0.06329	0.00289	0.6352	0.6372	5724/9011
	3	0.06375	0.00495	0.6411	0.6478	5895/9125

[a] R′ = Area of water peak/area n-pentane peak.

[b] R = (R′) (n-Pentane, gm/0.06309, gm). Corrects R′ to a common weight of internal standard.

[c] Bridge current: 180 ma; helium flow: 60 ml/min; initial column temperature: 105°C; sample size: 60 μl; attenuation: 8X; programmed temperature: 30°C/min.

[d] Bridge current: 177 ma; sample size: 100 μl; attenuation: 16X. R′ = area of water peak/area n-pentane peak.

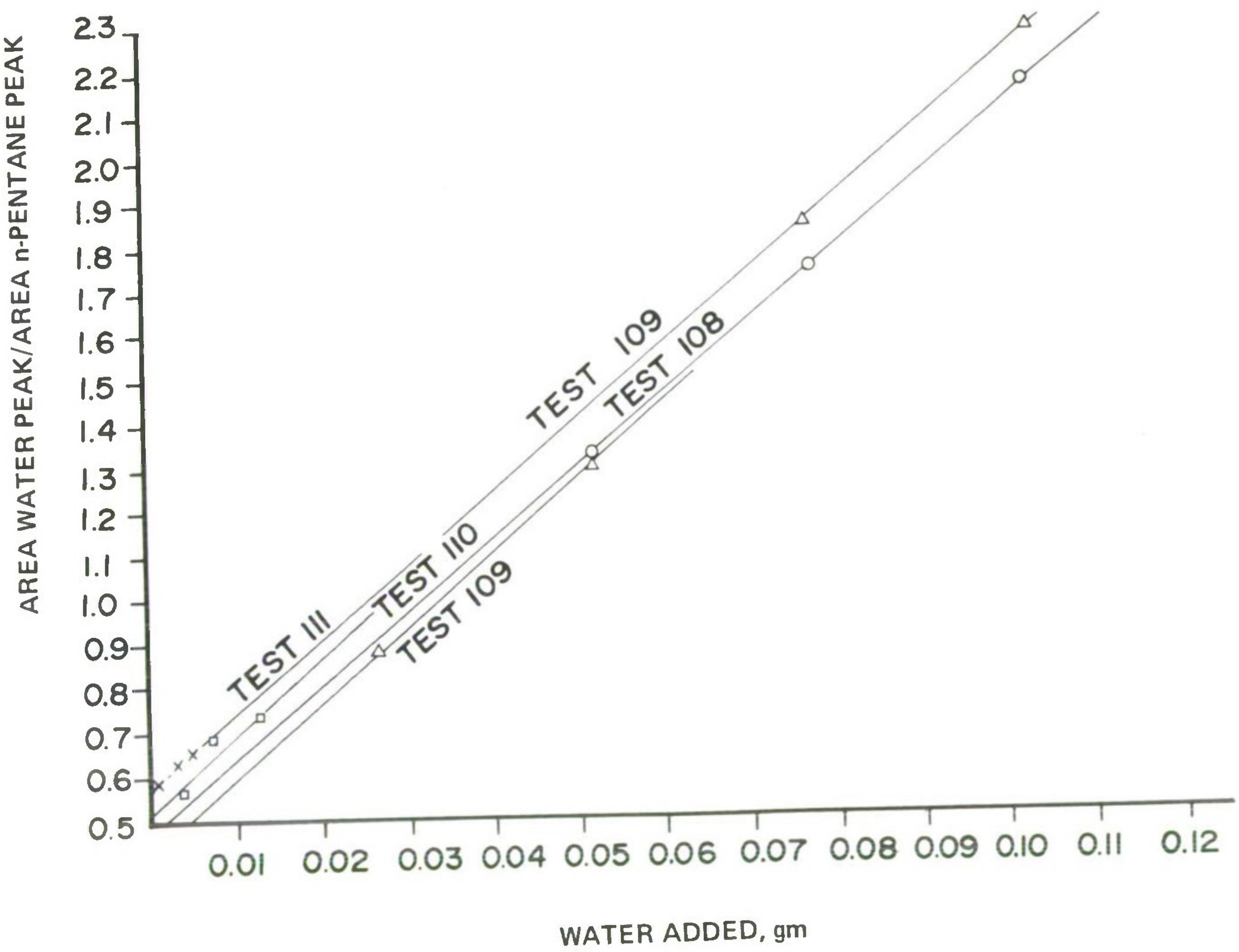

Figure 1. Water in Methanol/n-Pentane Internal Standard

Table II. Water in Methanol/Benzene Internal Standard

Test	Sample No.	Benzene	Water	R'[a]	R[b]	Area water peak / Area benzene peak
		gm	gm			
118[c]	2	0.04535	0.00222	0.8659	0.8730	10025/11577
	3	0.04516	0.00397	– –	– –	– –
	5	0.04504	0.00632	0.9867	0.9880	11302/11454
	10	0.04547	0.01247	1.1994	1.2125	13995/11668
	20	0.04501	0.02204	1.5189	1.5199	17282/11378
120[d]	1	0.04531	0.00101	0.5191	0.5229	7184/13837
	2	0.04532	0.00289	0.5939	0.5984	8106/13647
	3	0.04506	0.01006	0.8326	0.8341	11547/13868
	4	0.04486	0.01988	1.1760	1.1728	16026/13628

[a] R' = Ratio, area water peak/area benzene peak.

[b] R = R' X (grams of benzene/0.04498 grams of benzene). This procedure corrects R' to a common weight of benzene.

[c] Bridge current: 160 ma; helium flow: 40 ml/min; initial column temperature: 85°C; sample size: 60 μl; attenuation: 4X; programmed temperature: 30°C/min.

[d] Sample size: 70 μl. See footnote c (above) for other parameters.

Table III. Replicate Tests/Water in Methanol

Test No.	Sample No.[a]	R'[b]	R[b]	Area water peak / Area benzene peak	$\bar{R}_{119}$[c]	$\bar{R}_{118,119}$[d]
119–1	2	0.9003	0.9077	10615/11791		
119–2	2	0.8930	0.9003	10264/11493		
119–3	2	0.8861	0.8934	12002/13544		
119–4	2	0.9294	0.9370	13408/14427	0.9060	0.9023
119–1	3	0.9024	0.9060	10252/11361		No data for
119–2	3	0.9085	0.9122	12686/13963		test 118
119–3	3	0.9125	0.9166	12393/13575		
119–4	3	0.9359	0.9396	13690/14627	0.9186	0.9186
119–1	5	0.9862	0.9876	11464/11624		
119–2	5					
119–3	5	1.0373	1.0387	13572/13084		
119–4	5	1.0126	1.0140	14837/14652	1.0134	1.0071
119–1	10	1.1812	1.1940	13984/11839		
119–2	10	1.1891	1.2020	16308/13714		
119–3	10	1.1932	1.2062	16251/13620		
119–4	10	1.1927	1.2057	17496/14669	1.2020	1.2041
119–1	20					
119–2	20	1.5359	1.5369	21186/13794		
119–3	20	1.5221	1.5232	20476/13446		
119–4	20	1.5137	1.5147	21996/14531	1.5249	1.5237

[a] Standard samples from test 118 were used for test 119. See table II compositions.

[b] R' = Ratio, area water peak/area benzene peak.

[c] Average value of R for each sample.

[d] Average value of R for combined data from tests 118 and 119.

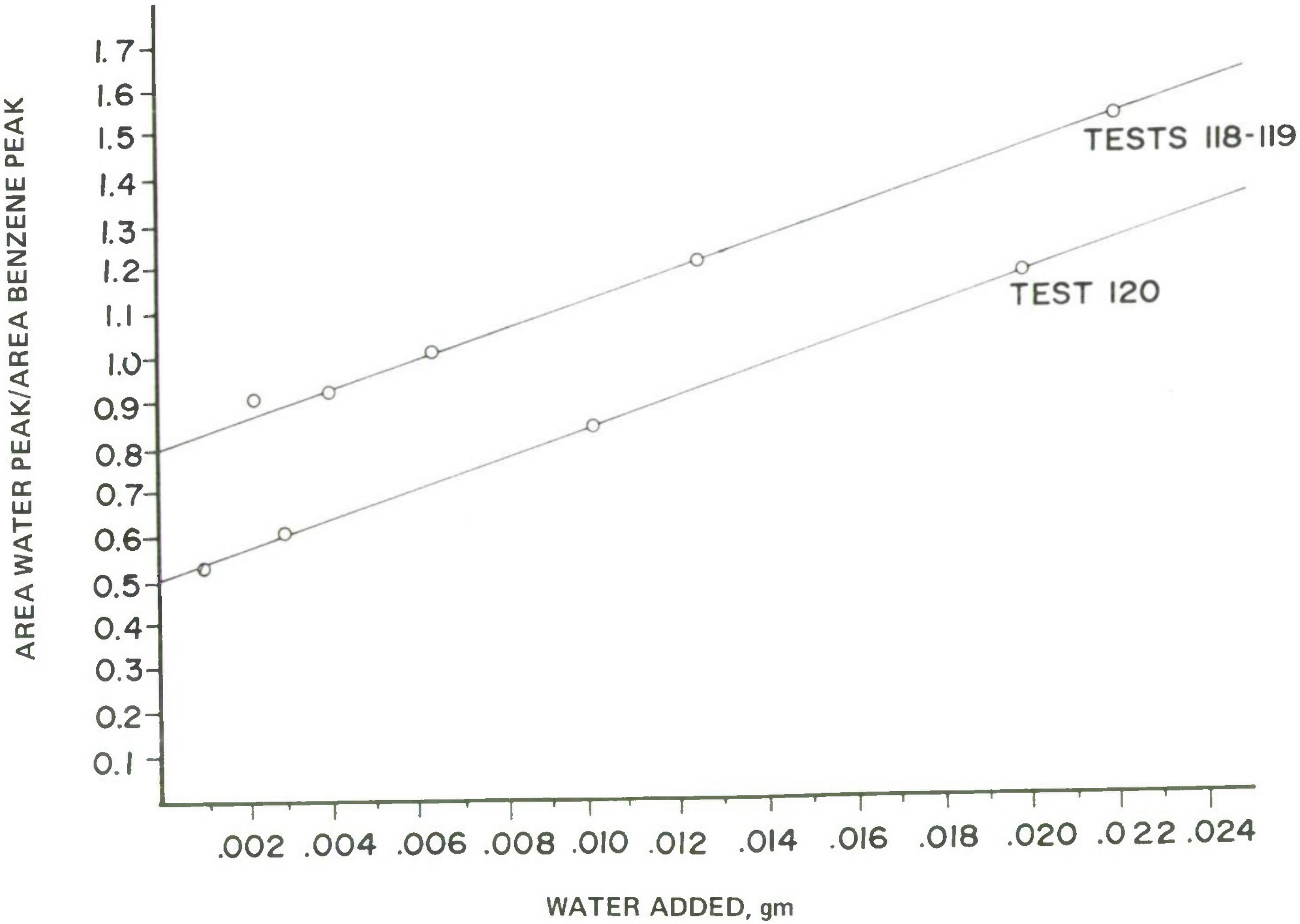

Figure 2. Water in Methanol/Benzene Internal Standard

anticipated from the lower water blank of the methanol used. Since tests 118 and 120 were run under similar chromatographic conditions, the combined data was fitted to a common regression curve. Methanol used to prepare standards for test 120 contained less water than that used in test 118. To put data from both tests on an "equal methanol water blank" basis, the equation of the regression curve was found for each test. The difference in value between the Y-intercepts of the two curves was added to each R value of test 120. These adjusted values of R and the respective values of X for test 120, along with pertinent data from test 118, are in table IV.

Table IV. Data for Individual Regression Curves

Test	Sample No.	Water (X)	R	$R+(a_{118}-a_{120})$[a]
		gm		
118[b]	2	0.00222	0.8730	–
	5	0.00632	0.9880	–
	10	0.01247	1.2125	–
	20	0.02204	1.5199	–
120[c]	1	0.00101	0.5229	0.8221
	2	0.00289	0.5984	0.8976
	3	0.01006	0.8341	1.1333
	4	0.01988	1.1728	1.4720

[a] a = Y-intercept when weight of water added equals zero grams.
$(a_{118}-a_{120}) = 0.2992$.

[b] Test 118 regression curve equation : $R = 0.7923041 + 33.0820845\ (X)$.

[c] Test 120 regression curve equation: $R = 0.4931397 + 34.1501589\ (X)$.

C. Regression Curve with Confidence Bands.

Values used to obtain the common regression curve (figure 3), 0.95 and 0.99 confidence bands are in table V. Calculations were made by following the procedures published by M. G. Natrella[2] of the National Bureau of Standards. (An OMNITAB program, subsequently written by Merrill E. Milham of this laboratory to perform these calculations, is in the appendix.)

A plot of the 0.99 confidence bands about the common regression curve (figure 3) indicated that the weight of water in a sample could be determined with an accuracy o of ±0.001 grams in the range of 0.001 to 0.022 grams of water.

D. Calculations.

In order to use a previously prepared standard curve (e.g., test 120, figure 2) to analyze a pyrotechnic sample, it is required that a new standard solution be prepared at the same time from methanol of the same water content as was used to extract water from the pyrotechnic sample. The ratio, R, of the new standard is used to draw a new curve either above or below and parallel to the original curve. The water in the sample is found by comparison of its R value to that of the adjusted curve. Percent of water in a mix may be calculated as follows:

$$\%\ \text{Water} = \frac{\text{weight of water in mix}}{\text{weight of pyrotechnic sample}} \times 100\%$$

This analysis presupposes that the chromatograph is functioning normally and that the same set of chromatographic conditions was used for test sample and standard as had been employed in preparation of the original curve.

Weight of water in a sample may be found also from the calculated slope of a two-point curve by determining the R values for two standard solutions of known water content.

Slope (S) may be defined as follows:

$$S = \frac{R_2 - R_1}{(X_2 + W_m) - (X_1 + W_m)}$$

$R_{1,2}$ – Previously defined

$X_{1,2}$ – Previously defined

W_m – Original water content of methanol (blank)

To determine the weight of water (X_x) in a mix, substitute its R_x value for either R_1 or R_2 in the slope equation. Rewrite the slope equation and solve it for X_x as follows:

$$X_x = \frac{R_x - R_1}{S} + X_1$$

[2] Natrella, Mary Gibbons. Experimental Statistics. NBS Handbook 91. pp 5-17. US Printing Office, Washington, DC 1963.

Table V. Regression Curve, 0.95 and 0.99 Confidence Bands for Combined Data

Test	Sample No.	Water (X)	$X-\bar{X}$	R_c	$\frac{1}{n}+\frac{(X-\bar{X})^2}{S_{xx}}$	$s_{R_c}^2$	s_{R_c}
		gm					
118	2	0.00222	-0.0073912	0.8670879	0.2456096	0.0000284	0.0053291
	5	0.00632	-0.0032912	1.0044972	0.1488568	0.0000172	0.0041472
	10	0.01247	0.0028588	1.2106111	0.1428926	0.0000165	0.0040620
	20	0.02204	0.0124288	1.5313446	0.4660647	0.0000540	0.0073484
120	1	0.00101	-0.0086012	0.8265354	0.2882427	0.0000334	0.0057792
	2	0.00289	-0.0067212	0.8895426	0.2246244	0.0000260	0.0050990
	3	0.01006	0.0004488	1.1298412	0.1294179	0.0000150	0.0038729
	4	0.01988	0.0102688	1.4589533	0.3578252	0.0000415	0.0064420

Test	Sample No.	W (0.95)	R_c +W (0.95)	R_c −W (0.95)	W (0.99)	R_c+W (0.99)	R_c −W (0.99)
118	2	0.0170863	0.8841742	0.8500016	0.0249046	0.8919925	0.8421833
	5	0.0132969	1.0177939	0.9912003	0.0193812	1.0238784	0.9851160
	10	0.0130237	1.2236348	1.1975874	0.0189830	1.2295941	1.1916281
	20	0.0235607	1.5549053	1.5077839	0.0343414	1.5656860	1.4970032
120	1	0.0185295	0.8450649	0.8080059	0.0270081	0.8535435	0.7995273
	2	0.0163486	0.9058912	0.8731940	0.0238293	0.9133719	0.8657133
	3	0.0124174	1.1422586	1.1174238	0.0180993	1.1479405	1.1117419
	4	0.0206546	1.4796079	1.4382987	0.0301055	1.4890588	1.4288478

NOTE:

R_c = Regression value of R corresponding to respective value of X.

$R_c = \bar{R} + b_1 (X-\bar{X})$
(R = Y in OMNITAB program)

$S_{xx} = \Sigma X^2 - (\Sigma X)^2/n$

$s_{R_c}^2 = s_R^2 (1/n + (X-\bar{X})^2/S_{xx})$

$\bar{X} = 0.0096112$; $\bar{R} = 1.1148000$; $s_R^2 = 0.0001160$; $n = 8$; $b_1 = 33.5144687$ (slope)

$S_{xx} = 0.0004527$; $b_o = 0.7926858$ (Y intercept of curve)

$W = \sqrt{2F}(s_{R_c})$; $F_{0.95}(2,6) = 5.14$; $F_{0.99}(2,6) = 10.92$

(Values for F were taken from table A-5, pp T-7, T-9, reference 2).

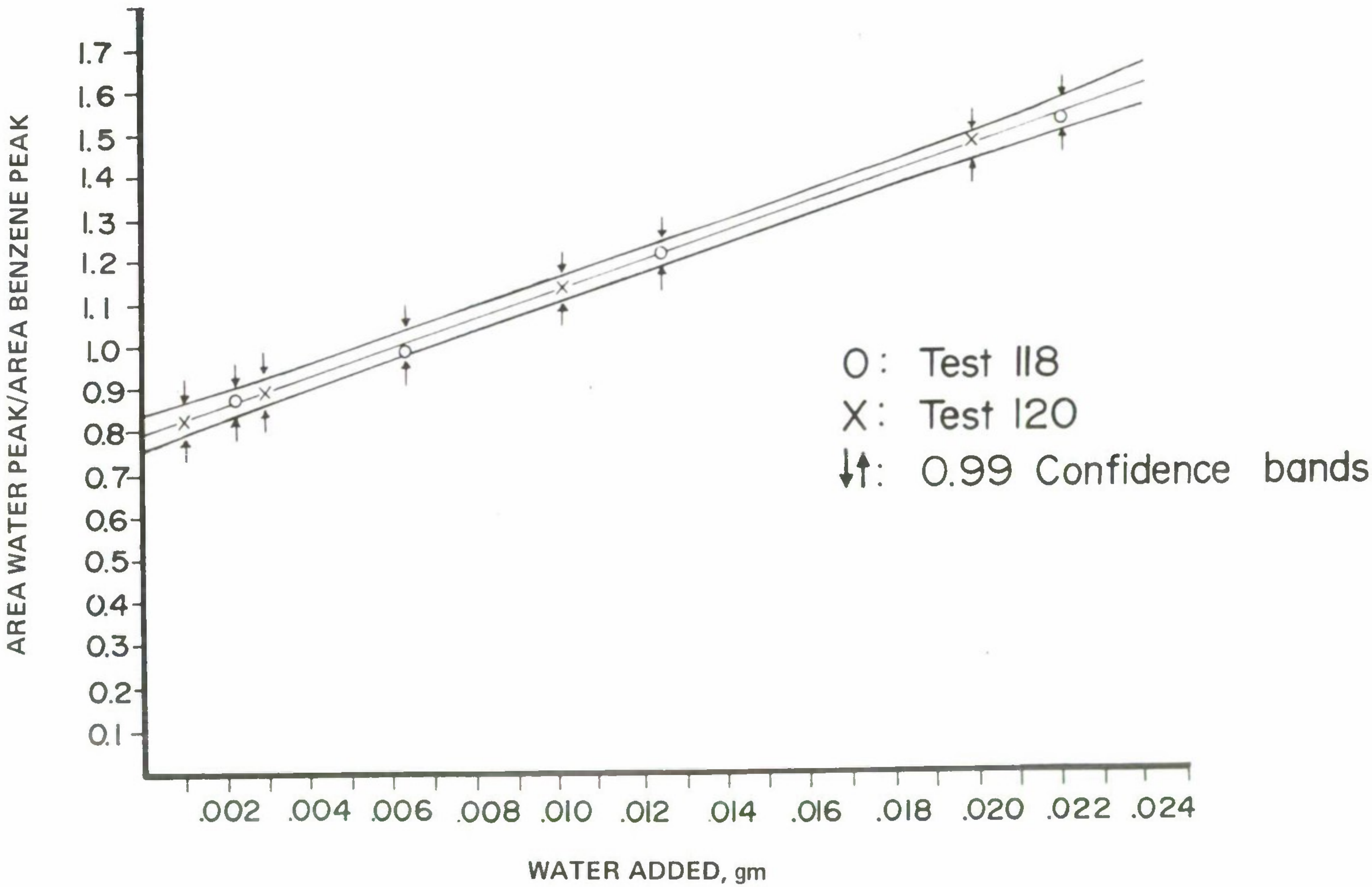

Figure 3. Water in Methanol/Benzene Internal Standard

To determine the water blank (W_m) of the methanol used for extraction, substitute above values of $X_{1,2}$ and $R_{1,2}$ into the following equation:

$$\frac{R_1}{X_1 + W_m} = \frac{R_2}{X_2 + W_m}$$

therefore

$$W_m = \frac{R_2 X_1 - R_1 X_2}{R_1 - R_2}$$

The value of W_m may be found also by drawing a line through the origin parallel to a standard curve. The distance between the two lines as measured on the "weight of water added" scale is a measure of the weight of water originally in the methanol.

IV. CONCLUSIONS.

Several facts indicate that accurate and reproducible results may be obtained by this procedure. When data from tests 118-119 and test 120 were plotted, the slopes of the curves obtained were very nearly parallel, as anticipated. (The difference in the initial water content of the methanol used prevented their coinciding.) Individual data points showed very good fit to the respective regression curves. The combined data from tests 118 and 120 showed a small deviation from a common regression curve.

The internal standard technique for the analysis of water appears to be a good general procedure for handling pyrotechnic mixtures. It is especially useful for the analysis of starter mixes that contain relatively little material, other than water, that is soluble in methanol. However, the method is also adaptable to mixes that contain methanol solubles in addition to water provided the chromatographic peaks of these materials do not overlap the water and internal standard peaks.

APPENDIX

OMNITAB: PROGRAM FOR REGRESSION ANALYSIS OF DATA AND CALCULATION OF CONFIDENCE BANDS.

By Merrill E. Milham

LIST OF COMMANDS, DATA AND DIAGNOSTICS

```
     HEAD COL4/ AVG X
     HEAD COL5/ AVG Y
     HEAD COL3/ NUMBER
     HEAD COL 14/ SLOPE
     HEAD COL 15/ INTERCEPT
     HEAD COL 19/ S.D. SLOPE
     HEAD COL 22/ S.D. INCPT
     HEAD COL 2/ Y DATA
     HEAD COL 25/ Y - W
     HEAD COL 16/ Y REG
     HEAD COL 24/ Y + W
     HEAD COL 1/ X DATA
     TITLEX    WEIGHT OF WATER
     TITLEY    PEAK AREA RATIO
     BEGIN STORING INSTRUCTIONS FOR LATER USE
 1   COUNT COL 1 PUT IN COL 3
 2   AVERAGE COL 1 PUT IN COL 4
 3   AVERAGE COL 2 PUT IN COL 5
 4   SUBTRACT COL 4 FROM COL 1 PUT IN COL 6
 5   SUBTRACT COL 5 FROM COL 2 PUT IN COL 7
 6   SQUARE COL 6 PUT IN COL 8
 7   SQUARE COL 7 PUT IN COL 9
 8   MULTIPLY COL 6 BY COL 7 PUT IN COL 10
 9   SUM COL 8 PUT IN COL 11
10   SUM COL 9 PUT IN COL 12
11   SUM COL 10 PUT IN COL 13
12   DIVIDE COL 13 BY COL 11 PUT IN COL 14
13   MULTIPLY COL 4 BY COL 14 PUT IN COL 15
14   SUBTRACT COL 15 FROM COL 5 PUT IN COL 15
15   MULTIPLY COL 1 BY COL 14 PUT IN COL 16
16   ADD COL 15 TO COL 16 PUT IN COL 16
17   SQUARE COL 13 PUT IN COL 17
18   DIVIDE COL 17 BY COL 11 PUT IN COL 17
19   SUBTRACT COL 17 FROM COL 12 PUT IN COL 17
20   DEFINE 2.0 INTO COL 18
21   SUBTRACT COL 18 FROM COL 3 PUT IN COL 18
22   DIVIDE COL 17 BY COL 18 PUT IN COL 17
23   DIVIDE COL 17 BY COL 11 PUT IN COL 19
24   SORT COL 19 PUT IN COL 19
```

LIST OF COMMANDS, DATA AND DIAGNOSTICS

```
 25  DEFINE 1.0 INTO COL 21
 26  DIVIDE COL 21 BY COL 3 PUT IN COL 21
 27  SQUARE COL 4 PUT IN COL 22
 28  DIVIDE COL 22 BY COL 11 PUT IN COL 22
 29  ADD COL 21 TO COL 22 PUT IN COL 22
 30  MULTIPLY COL 22 BY COL 17 PUT IN COL 22
 31  SORT COL 22 PUT IN COL 22
 32  DIVIDE COL 8 BY COL 11 PUT IN COL 23
 33  ADD COL 21 TO COL 23 PUT IN COL 23
 34  ADD COL 20 TO COL 20 PUT IN COL 20
 35  MULTIPLY COL 23 BY COL 17 PUT IN COL 23
 36  MULTIPLY COL 23 BY *1,20* PUT IN COL 23
 37  SORT COL 23 PUT IN COL 23
 38  ADD COL 23 TO COL 16 PUT IN COL 24
 39  SUBTRACT COL 23 FROM COL 16 PUT IN COL 25
 40  PRINT COL 3, 4, 5, 14, 15, 19, 22
 41  NEW PAGE
 42  PRINT COL 1, 2, 25, 16, 24
 43  PLOT COL 2, 16, 24, 25 VS COL 1
   FINISH STORING INSTRUCTIONS FOR LATER USE
   SET IN COL 1 X
   0.00222, 0.00632, 0.01247, 0.02204, 0.00101, 0.00289, 0.01006, 0.01988
   SET IN COL 2 Y
   0.8730, 0.9883, 1.2125, 1.5199, 0.8221, 0.8976, 1.1333, 1.4720
   SET IN COL 20
   5.14
   PERFORM 1 THRU 43
   SET IN COL 20
   10.92
   PERFORM 1 THRU 43
   STOP
```

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